PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-004087
(43)Date of publication of application : 09.01.2002

(51)Int.Cl.
C25D 11/12
B82B 1/00
B82B 3/00
C25D 11/04
C25D 11/16

(21)Application number : 2000-187668
(22)Date of filing : 22.06.2000

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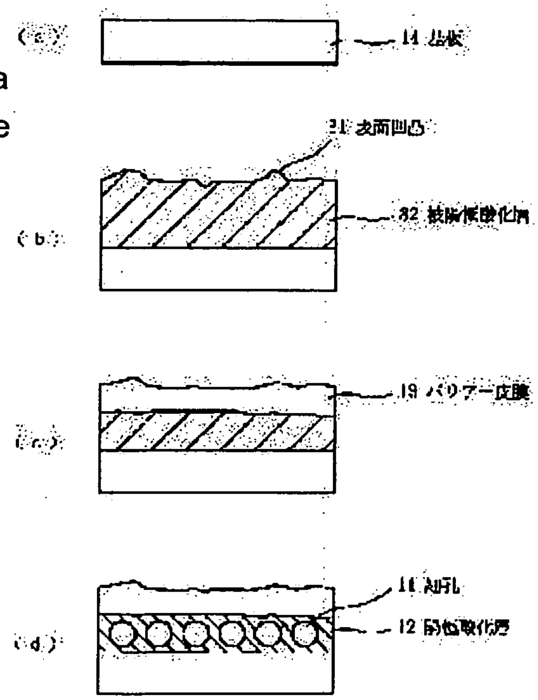
(54) METHOD FOR MANUFACTURING NANOSTRUCTURE AND NANOSTRUCTURE

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a method for manufacturing a more regular nanostructure by lessening the disorder and defect made by anodic oxidation.
SOLUTION: In the method for manufacturing the nanostructure which anodically oxidizes a layer to be anodically oxidized essentially consisting of Al to form pores, a barrier film is formed by anodic oxidation on the surface of the layer to be anodically oxidized, and after the forming positions of the pores are positioned by removing at least part of the barrier film, the porous film by the anodic oxidation is manufactured.



LEGAL STATUS
[Date of request for examination]
[Date of sending the examiner's decision of rejection]
[Kind of final disposal of application other than the examiner's decision of rejection or application

converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

CLAIMS

[Claim(s)]
[Claim 1] The manufacture approach of the nano structure characterized by to produce the porous coat by anodic oxidation in this anodized layer after removing this anodized layer or this barrier layer under this barrier layer in the manufacture approach of the nano structure which is made to anodize the anodized layer which uses aluminum as a principal component, and forms pore after producing a barrier coat by anodic oxidation on the front face of this anodized layer.
[Claim 2] The manufacture approach of the nano structure according to claim 1 which produces a porous coat after producing this barrier coat, and removing this a part of barrier coat [at least].
[Claim 3] The manufacture approach of the nano structure according to claim 2 that the removal part of this barrier coat supports the formation location of pore.
[Claim 4] The manufacture approach of the nano structure according to claim 2 which produces a pore formation start point after removing this barrier coat.
[Claim 5] The manufacture approach of the nano structure according to claim 2 which produces a porous coat after removing this barrier coat, and forming an insulating layer in the front face of this anodized layer.
[Claim 6] The manufacture approach of the nano structure according to claim 5 which produces a porous coat after removing the part corresponding to the formation location of the pore of this insulating layer.
[Claim 7] The manufacture approach of the nano structure according to claim 1 or 5 which produces the porous coat which is aluminum film with which this anodized layer was formed on the substrate, and this substrate front face is insulation, and has pore parallel to this substrate.
[Claim 8] The manufacture approach of the nano structure given in claim 1 which produces the porous coat which this anodized layer is aluminum film formed on the substrate, and has pore perpendicular to this substrate thru/or one term of 4.
[Claim 9] The nano structure produced by the manufacture approach according to claim 1 to 8.
[Claim 10] The process which prepares the layer which is the manufacture approach of the pore which is made to anodize the layer which uses aluminum as a principal component, and forms pore, and uses aluminum as a principal component, The 1st anodic oxidation process which advances anodic oxidation in the 1st direction to the layer which uses this aluminum as a principal component, this -- the 1st anodic oxidation process -- then, the manufacture approach of the pore characterized by having the 2nd anodic oxidation process which advances anodic oxidation of the layer which uses said aluminum as a principal component in the different direction from said 1st direction.
[Claim 11] The process which prepares the layer which uses said aluminum as a principal component is the manufacture approach of the pore according to claim 10 characterized by being the process which arranges the film which uses aluminum as a principal component on the 1st [of a substrate] principal plane.
[Claim 12] Said 2nd anodic oxidation process is the manufacture approach of the pore according to claim 11 characterized by being the process which forms pore, oxidizing the layer which uses said aluminum as a principal component.
[Claim 13] Said 1st direction is the manufacture approach of the pore according to claim 11 or 12 characterized by being a perpendicular direction substantially to said 1st principal plane.
[Claim 14] Said 2nd direction is the manufacture approach of the pore according to claim 13 characterized by being an parallel direction substantially to said 1st principal plane.

[Translation done.]

* NOTICES *

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1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] The nano structure possessing the pore object from which especially this invention is obtained by the manufacture approach of this invention about the manufacture approach of the nano structure and the nano structure is available in the range large as an optical device besides an electron device, a magnetic device, and the quantum effectiveness device, a micro device, a three-dimensional structure ingredient, etc.
[0002]
[Description of the Prior Art] In a <nano structure> metal and the thin film of a semi-conductor, a thin line, and a dot, there is a unique thing for which electric, optical, and chemical property are shown by shutting up a motion of an electron in size smaller than a certain characteristic die length. The interest of the ingredient (nano structure) which has structure more detailed than several 100 nanometers (nm) as high-performance material from such a viewpoint is increasing.
[0003] As the manufacture approach of the nano structure, photolithography is begun and production by semi-conductor processing techniques including detailed pattern drawing techniques, such as electron beam lithography and X-ray lithography, is raised, for example.
[0004] Moreover, the attempt which is going to realize the new nano structure is in ** 1 SU in the regular structure formed automatically, i.e., the structure formed in a self-regulation target, besides such a producing method. Since such technique may be able to produce the detailed and special structure which turns around the conventional approach a top depending on the fine structure used as BE 1 SU, many researches are beginning to be done.
[0005] The anodic oxidation which can produce easily the nano structure which has the pore of nano size with sufficient control as such self-regular technique is mentioned. For example, the anodic oxidation alumina which produces aluminum and its alloy by anodizing in an acid bath is known. Hereafter, an anodic oxide film is explained in detail.
[0006] < anodic-oxidation alumina: If >aluminum plate is anodized in the acid electrolytic solutions, such as a sulfuric acid, oxalic acid, and phosphoric acid, about a porous coat, a porosity oxide film (porous mold anodic oxide film: abbreviate to a porous coat henceforth) will be formed (for example, reference, such as R.C.Furneaux, W.R.Rigby&A.P.Davidson"NATURE"Vol.337, and P147 (1989)). Drawing 9 is the sectional view showing the nano structure which has the vertical mold pore of the conventional example. Drawing 9 (a) is a top view and drawing 9 (b) is CC' line sectional view.
[0007] As shown in drawing 9 , the very detailed cylindrical pore (nano hole) 11 whose diameter 2r is several nm - hundreds of nm has the description of this porous coat in having the specific geometric structure of arranging in parallel by spacing of dozens of nm - hundreds of nm 2R (cell size). The pore 11 of the shape of this cylinder has a high aspect ratio, and is excellent also in the uniformity of the path of a cross section. Although the insulating layer called a barrier layer is formed in the bottom of this pore 11, in order to distinguish from the anodic oxidation coatings (barrier coat) of the barrier mold which is the anodic oxidation coatings which do not form pore clearly, by this invention, the barrier layer of the bottom of pore 11 is only called a pore bottom insulating layer.
[0008] Moreover, a certain amount of control is possible by changing the conditions of anodic oxidation of the structure of a porous coat. For example, the thing controllable to some extent is known [depth / of pore / pore size] for

anodic oxidation time amount by pore wide processing in pore spacing on the anodic oxidation electrical potential difference.
[0009] Moreover, in order to improve the perpendicularity, the linearity, and the independence of pore of a porous coat Once removing the approach, i.e., the porous coat which formed by performing anodic oxidation, of performing two steps of anodic oxidation, it anodizes again. Better perpendicularity, linearity, An independence The shown pore The approach of producing the porous coat which it has is proposed ("Japanese Journal of Applied Phisics", Vol.35, Part2.No.1B, pp.L126-L129, 15 January 1996). Here, this approach uses that the hollow of the front face of aluminum plate made when removing the anodic oxide film formed by the first anodic oxidation serves as a formation start point of the pore of the 2nd anodic oxidation.
[0010] In order to improve the controllability of the configuration of the pore of a porous coat, spacing, and a pattern furthermore It anodizes, after forming the hollow which forces on the front face of aluminum plate the approach of forming the formation start point of pore using a stamper, i.e., the substrate which equipped the front face with two or more projections, and can do it as a formation start point of pore. The approach of producing the porous coat which has the pore which shows the controllability of a better configuration and a spacing **** pattern is also proposed (Nakao JP,10-121292,A or Masuda "solid-state physics" 31,493 (1996)). Moreover, the technique which forms pore in concentric circular [instead of a honeycomb] is reported by Okubo and others by JP,11-224422,A.
[0011] Otherwise, aluminum film inserted with the insulator is anodized in the direction of a film surface, and the example which produced pore to seriate is reported by Masuda and others ("Appl.Phys.Lett." 63, p3155 (1993)).
[0012] Various application which paid its attention to the specific geometrical structure of this anodic oxidation alumina is tried. Although the description by Masuda is detailed, an application is listed hereafter. For example, the application and the coat as a coat using the abrasion resistance of an oxide film on anode and insulation-proof are exfoliated, and there is application to a filter. Furthermore, various application including coloring, a magnetic-recording medium, EL light emitting device, an electrochromic element, an optical element, a solar battery, and a gas sensor is tried from using the technique filled up with a metal, a semi-conductor, etc. in pore, and the replica technique of pore. Furthermore, the application to the directions of many, such as the quantum effectiveness devices, such as quantum wire and an MIM component, and a molecule sensor using pore as a chemical reaction place, is expected (Masuda "solid-state physics" 31,493 (1996)).
[0013] < anodization alumina: If >aluminum plate is anodized in the electrolytic solutions, such as boric-acid AMMORIUMU, about a barrier mold coat, the barrier mold anodic oxidation coatings (it abbreviates to a barrier coat henceforth) of the shape of different film from porosity will be formed (for example, Kobayashi: refer to "surface technical" Vol.40, No12, and P10.1989 grade). The description of this barrier coat is formed by the thickness for which the precise oxidation insulating layer which does not have pore as compared with a porous coat depended on the electrical potential difference, and that thickness is (electrical-potential-difference V) x1.3 (nm) extent in general. Although an amorphous-like alumina is a principal component, as for the structure of this insulating layer, a crystalline alumina may be formed in part. A crystalline alumina is generated, and in order to make it there be nothing, there is the need of using the ammonium dihydrogenphosphate which is the electrolytic solution which a crystalline alumina cannot generate easily.
[0014]
[Problem(s) to be Solved by the Invention] Generally the alumina pore described previously is formed in aluminum plate front face, and the direction of pore has become a front face perpendicularly. However, processing to which aluminum substrate usually has intense irregularity and flattening of the aluminum front face is carried out by electrolytic polishing is performed in many cases. However, flattening sufficient in electrolytic polishing is difficult, and has the need of grinding aluminum of remarkable thickness by electrolytic polishing further. Especially the thing for which only the thickness which can carry out electrolytic polishing is secured not by aluminum plate but by formed aluminum film is difficult. By aluminum film, the heights generally called the crevice in a grain boundary and a hillock tended to be made, and a technique of flattening was desired.
[0015] Moreover, as mentioned above, the technique of producing pore in parallel with a substrate was also reported, but since the insulating layer was formed after forming aluminum, the interface of aluminum which is an anodized layer, and an insulating layer is confused by the grain boundary or the hillock, and had become the factor which disturbs the configuration of pore.

[0016] The purpose of this invention is offering the manufacture approach of the nano structure which lessens turbulence and the defect of the pore produced by anodic oxidation in view of these troubles. Moreover, the purpose of this invention is offering the manufacture approach of the nano structure incorporating the flattening technique of aluminum layer which lessens aluminum part made into a sacrifice by electrolytic polishing. Moreover, the purpose of this invention is offering the manufacture approach of the nano structure which has more regular pore. Furthermore, the purpose of this invention is offering the more regular nano structure with few turbulence of pore and defects.
[0017]
[Means for Solving the Problem] The above-mentioned technical problem is solvable with the following configurations and processes of this invention. That is, in the manufacture approach of the nano structure which is made to anodize the anodized layer which uses aluminum as a principal component, and forms pore, after producing a barrier coat on the front face of this anodized layer, it is the manufacture approach of the nano structure characterized by producing a porous coat in this anodized layer after removing this anodized layer or this barrier layer under this barrier layer.
[0018] Here, after producing this barrier coat, and removing a part of barrier coat [at least], the approach of producing a porous coat is also effective. In this case, after removing the manufacture approach that the removal part of this barrier coat supports the formation location of pore, or a barrier coat, removing the approach of producing a pore formation start point, or a barrier coat, and forming an insulating layer in the front face of an anodized layer, the approach of producing a porous coat is desirable. In the approach using this insulating layer, after removing the insulating layer of the part corresponding to the formation location of pore, the approach of producing a porous coat is also effective.
[0019] Moreover, it is aluminum film with which the anodized layer was formed on the substrate, and a substrate front face is insulation, and the manufacture approach of the nano structure which produces the porous coat which has pore parallel to a substrate is also effective. Moreover, an anodized layer is aluminum film formed on the substrate, and it is the manufacture approach of the nano structure which produces the porous coat which has pore perpendicular to this substrate.
[0020] Furthermore, the nano structure which has the pore produced by these manufacture approaches is peculiar to the manufacture approach, and is the structure useful as device application.
[0021] Moreover, the process which prepares the layer which this invention is the manufacture approach of the pore which is made to anodize the layer which uses aluminum as a principal component, and forms pore, and uses aluminum as a principal component, The 1st anodic oxidation process which advances anodic oxidation in the 1st direction to the layer which uses this aluminum as a principal component, this -- the 1st anodic oxidation process -- then, said 1st direction is the manufacture approach of the pore characterized by having the 2nd anodic oxidation process which advances anodic oxidation of the layer which uses said aluminum as a principal component in the different direction.
[0022] As for the process which prepares the layer which uses said aluminum as a principal component, it is desirable that it is the process which arranges the film which uses aluminum as a principal component on the 1st [of a substrate] principal plane. Moreover, it is desirable that it is the process which forms pore, said 2nd anodic oxidation process oxidizing the layer which uses said aluminum as a principal component. Moreover, as for said 1st direction, it is desirable that it is a perpendicular direction substantially to said 1st principal plane. Moreover, as for said 2nd direction, it is desirable that it is an parallel direction substantially to said 1st principal plane.
[0023] Next, in order to explain an operation of this invention, drawing 6 and drawing 7 are first used and explained about the conventional technique. It is drawing in which drawing 6 shows the conventional example of the anodic oxidation pore of a horizontal type, and drawing 7 shows the conventional example of the anodic oxidation pore of a vertical mold here. Heights, such as an anodized layer which the anodic oxidation layer which 11 in drawing uses an alumina as pore (nano hole), and 12 uses as a principal component, and 14 use aluminum as a substrate, and 32 uses as a principal component, and a hillock as which a pore bottom insulating layer and 62 are seen by the up insulating layer, and 71 is regarded for 61 on an anodized layer front face, and 72 are crevices, such as a grain boundary of an anodized layer, and a crack.
[0024] The vertical mold porous coat which is the most general conventional example is shown in drawing 7 . Drawing 7 (a) is the sectional view of the anodized layer before anodic oxidation, and drawing 7 (b) expresses the sectional view of the porous coat after anodic oxidation here. Although it is dependent also on the **** approach, the aluminum film which formed membranes has the inclination for the irregularity on the front face of the film as shown in drawing 7 (a)

to become large, so that the thickness generally becomes thick.
[0025] And if this aluminum film is made into an anode plate and it anodizes in acid solutions, such as a sulfuric acid, oxalic acid, and phosphoric acid, the front face of aluminum film will begin to oxidize. Under the present circumstances, since oxidization of aluminum film and etching of a specific part advance, pore 11 begins to be formed into the anodic oxidation layer 12. Although this pore is perpendicularly formed in general in a front face, the branching phenomenon in which growth of a part of pores stops on the way, or pore is divided occurs. Especially in the part which has irregularity in a front face, it is easy to become the disordered structure as such a defect become easy to generate and shown in drawing 7 (b).
[0026] It sees also with the porous anodic oxide film of a horizontal type which the same thing showed by drawing 6 . Drawing 6 (a) is drawing which cut near the center of an anodic oxidation layer in parallel with the field of an anodic oxidation layer, i.e., drawing cut in the location of B-B' of drawing 6 (b), and drawing 6 (b) expresses the sectional view in the location of A-Ain drawing 6 (a)' here. Where the anodized layer which was shown by a diagram and which is the thin film of aluminum like is pinched by the insulating layer, it is anodized and formed from one edge. namely, -- first -- the insulating substrate 14 top -- the case of aluminum layer and the vertical mold which carried out point ** of the pore when the up insulating layer 62 was further formed on it, it anodized from the edge of these cascade screens and the pore of a horizontal type was produced -- the same -- turbulence -- easy -- pore -- on the way -- disappearance and branching tend to take place. This turbulence will tend to increase, if irregularity is in aluminum film. The pore bottom insulating layer 61 exists between the anodized layer 32 which is not anodized yet by a diagram and pore, and this interface is also confused reflecting turbulence of pore.
[0027] When he inquired wholeheartedly that this turbulence should be canceled, this invention person etc. was forming a porous coat, after forming the barrier coat in the front face of an anodized layer, and turbulence and a defect could be lessened and he did the thing header.
[0028] This operation is first explained using drawing 5 about the porous coat of the above-mentioned horizontal type. Drawing 5 is drawing showing the making process of a horizontal-type pore object. 31 is surface irregularity and 13 is a barrier coat here. First, the surface irregularity 31 exists in the aluminum front face which was shown by drawing 5 (b) and which is the anodized layer 32 after membrane formation like. Next, if it anodizes in the solution which forms barrier coats, such as ammonium pentaborate, only the thickness for which the barrier coat 13 depended on anodization conditions will be formed in the front face of the anodized layer 32 like drawing 5 (c). Under the present circumstances, the interface of the anodized layer 32 which remained, and the barrier coat 13 serves as flat structure as compared with the irregularity of anodized layer 32 front face before anodization. And if the anodized layer 32 which remained is anodized in the solution which can do a porous coat from a cross section, as shown in drawing 5 (d), the pore of a horizontal type with little turbulence will be formed.
[0029] The same effectiveness is seen also by the porous coat of a vertical mold. In this case, it attaches and explains using drawing 3 . Drawing 3 is drawing showing the making process of the vertical mold pore object from which the barrier coat was removed. First, the surface irregularity 31 exists in the aluminum front face which was shown by drawing 3 (b) and which is the anodized layer 32 after membrane formation like. Next, if it anodizes in the solution which forms barrier coats, such as ammonium pentaborate, only the thickness for which the barrier coat 13 depended on anodization conditions will be formed in the front face of the anodized layer 32 like drawing 3 (c). Under the present circumstances, the interface of the anodized layer 32 which remained, and the barrier coat 13 serves as flat structure as compared with the irregularity of anodized layer 32 front face before anodization. Next, if the surface barrier coat 13 is removed by technique, such as etching, the anodized layer 32 which has a flat front face will remain, and it will become drawing 3 (d). And if the anodized layer 32 which remained is anodized in the solution which can do porous one, as shown in drawing 3 (e), the pore of a vertical mold with little turbulence will be formed.
[0030]
[Embodiment of the Invention] the pore of a horizontal type and a vertical mold -- a case -- dividing -- carrying out -- an operative condition -- it attaches like and explains.
<the manufacture approach of horizontal-type pore> -- a configuration as shown in drawing 2 as simplest example of a configuration is mentioned. Drawing 2 is the sectional view showing the nano structure which has the horizontal-type pore of this invention, and, as for a sectional view in case the number of porous coats is one, and drawing 2 (b), the porous coat of drawing 2 (a) is a sectional view in the case of being two-layer. Drawing 2 R> 2 (a) is a configuration

with the anodic oxidation layer 12 which is the porous coat which has the substrate 14 which functions as an insulating layer on a substrate 14, and the pore 11 pinched by the barrier coat 13. Drawing 2 (b) is a configuration which has the anodization layer 12 and the up barrier coat 22 in the upper part further. 21 in drawing is a middle barrier coat, and 22 is an up barrier coat.
[0031] Here, the process which produces the configuration of drawing 2 (a) is explained using drawing 5 .
(1) When producing horizontal-type pore about a substrate, it is desirable that a substrate front face is insulation. An insulating substrate may be used, and this is not cared about even if it uses the substrate in which the insulating layer was formed on the conductive substrate. The ingredient which neither corrosion nor the dissolution generates as this insulating ingredient at the time of anodizing is desirable. Moreover, if irregularity exists in this insulating layer, since it will lead to turbulence and the defect of pore, a flat thing is desirable.
[0032] (2) Although aluminum is generally used as an anodized layer about production of an anodized layer, other elements may be contained as long as it can anodize aluminum by the film used as a principal component. The vacuum deposition method by resistance heating, the sputtering method, a CVD method, etc. can be used for membrane formation of this aluminum. However, it is not desirable if it is not the approach of forming the film which has a to some extent flat front face. However, by any approaches other than epitaxial growth, it is not avoided that surface irregularity as shown in drawing 5 (b) occurs. Although there is especially no limit in the thickness of the anodized layer to produce, if the path of pore is taken into consideration, several micrometers are suitable from several 10nm. Of this process, the layer 32 which uses aluminum as a principal component is formed on the 1st [of a substrate 14] principal plane.
[0033] (3) It is necessary to anodize in a specific solution in production of the barrier coat by anodization about production of a barrier coat. As a desirable solution, an ammonium pentaborate solution, a tartaric-acid solution, etc. are mentioned. When a crystalline alumina is made and a bad influence appears in the surface smoothness of a front face or an interface, it is also effective to use the ammonium dihydrogenphosphate which is the electrolytic solution which a crystalline alumina cannot generate easily.
[0034] The equipment shown by drawing 8 can perform anodic oxidation. That is, the reaction container 84 is installed into the incubator 87 as for which temperature is made to regularity, and the electrolytic solution 83 is moderately filled in a reaction container. The cathode 82 which is the sample 81 and counter electrode which are anodized there is installed, and an electrical potential difference is made to impress between a sample and a counter electrode according to a power source 85. In this 1st anodic oxidation process, anodic oxidation advances in the perpendicular direction substantially to the 1st principal plane of a base 14. The approach of generally carrying out armature-voltage control for production of a barrier coat is taken. The thickness of a barrier coat is (electrical-potential-difference V) x1.3 (nm) extent in general, as it mentioned above, although it was dependent also on conditions. Although an amorphous-like alumina is a principal component, as for the structure of this insulating layer, a crystalline alumina may be formed in part. Since the interface of a barrier coat and an anodized layer tends to become flat, it is effective in lessening turbulence and the defect of the pore in a porous coat.
[0035] After forming a barrier coat, a porous coat may be produced, but on device production, in the case which is not desirable, after using a barrier coat removes a barrier coat, even if it produces another insulating layer instead of a barrier coat, it does not matter. Even in this case, the irregularity of the front face of an anodized layer is controlled as compared with early irregularity, and since flattening is carried out, the effectiveness of this invention is acquired. Although the mixed solution of a chromic acid and phosphoric acid can be used for this etching processing, etching using other plasma and ion may be used.
[0036] (4) As for the electrolytic solution used for anodic oxidation about production of a porous coat, oxalic acid, phosphoric acid, a sulfuric acid, a chromic-acid solution, etc. are mentioned. Terms and conditions, such as an anodic oxidation electrical potential difference and temperature, can be suitably set up according to the nano structure to produce. Generally, by the low battery not more than 30V, an anodic oxidation electrical potential difference is used by the sulfuric-acid bath and the high voltage beyond 80V, and an oxalic acid bath is used in a phosphoric acid bath and an electrical potential difference in the meantime in many cases. It is effective to perform processing which starts the cross section anodized so that turbulence may not appear in the initial process of anodic oxidation before anodic oxidation. There are the approach of carrying out patterning of an anodized layer and the barrier layer by the photolithography method, the approach of cutting from a substrate using the cleavage plane of a substrate, etc. in this. According to this

2nd anodic oxidation process, anodic oxidation advances in the parallel direction substantially to the 1st principal plane of a substrate. And in this 2nd anodic oxidation process, the oxidation of a layer and the formation of pore which use aluminum as a principal component are performed. Moreover, the depth direction of pore 11 is substantially formed in the parallel direction to the 1st principal plane of a substrate of said 1st anodic oxidation and the 2nd anodic oxidation process.
[0037] By processing which dips the above-mentioned pore object into acid solutions, such as a phosphoric acid solution, after anodic oxidation, pore size can be extended suitably. It can consider as the nano structure which has desired pore size by adjusting acid concentration, the processing time, and temperature. What is necessary is just to repeat processing of the above (2), (3), and (4) in production of a porous layer multistage as shown in drawing 2 (b).
[0038] <the manufacture approach of vertical mold pore> -- a configuration as shown in drawing 1 as simplest example of a configuration is mentioned. Drawing 1 is the sectional view showing the nano structure which has the vertical mold pore of this invention. Drawing 1 (a) is a configuration with the anodic oxidation layer 12 which is a sectional view in the condition of having left the barrier coat, and is the porous coat which has pore 11 under a barrier coat. Drawing 1 (b) is the sectional view of a configuration of having removed the barrier coat. Here, the process which produces the configuration of drawing 1 is explained using drawing 3 and drawing 4 .
[0039] (1) When producing vertical mold pore about a substrate, a substrate front face does not need to be insulation. Conversely, in order even for a substrate to make pore reach, a conductive substrate or the substrate which produced the conductive film on the front face is required. As this conductive ingredient, semi-conductors, such as metals, such as bulb metals, such as Ti, Nb, W, Zr, and Hf, and Pt, Cu, these alloys, and Si, are mentioned. However, if irregularity exists in this conductive layer, since it will lead to turbulence and the defect of pore, a flat thing is desirable.
[0040] (2) An anodized layer is produced like [in the first half] the case of horizontal-type pore about production of an anodized layer. However, since the die length of pore can be determined by thickness, it is necessary to give the thickness doubled with desired pore length. If actual aluminum membrane formation is taken into consideration, several 10 micrometers is suitable for thickness from several 10nm. Little direction of the surface irregularity of an anodized layer is desirable like [in the first half] the case of horizontal-type pore.
[0041] (3) It is produced like [production / of a barrier coat / production of the barrier coat by anodization] the case of said horizontal-type pore. However, the various approaches are mentioned to a subsequent process. For example, there are the following approaches.
[0042] a) How to remove a barrier coat and produce a porous coat, after forming a barrier coat.
After removing a barrier coat by etching etc., it is the approach shown in drawing 3 which forms a porous coat by anodic oxidation. Also in this case, the irregularity of the front face of an anodized layer is controlled as compared with early irregularity, and since flattening is carried out, the effectiveness of this invention is acquired. In this case, it is also effective after etching of a barrier coat to produce the crevice used as the start point of pore formation on an anodized layer front face etc. the approach according to photolithography in production of a crevice, the interference exposing method, and FIB (Focused Ion Beam) -- law, the stamp method, etc. are mentioned.
[0043] b) How to produce a porous coat, after removing a barrier coat partially.
In order to leave a barrier coat and to form a porous coat, it is required to remove partially the barrier coat which is an insulating layer. In this case, it is desirable to produce periodically the removal part 41 corresponding to the location of the pore which it is going to produce in a porous layer like shown in drawing 4 (d), and to consider as a start point.
[0044] c) How to produce a porous coat, after removing a barrier coat, and forming another insulating layer.
After leaving a barrier coat removes a barrier coat on device production in the case which is not desirable, another insulating layer may be produced instead of a barrier coat. In this case, since an insulating layer is shown in a front face, it is desirable to produce periodically the removal part 41 corresponding to the location of the pore which it is going to produce in a porous layer like shown in the insulating layer at drawing 4 (d) for formation of a porous layer, and to consider as a start point.
[0045] Although the mixed solution of a chromic acid and phosphoric acid can be used for the above-mentioned etching processing, etching using other plasma and ion may be used.
[0046] Although it will not matter anything as an insulating layer used instead of the above-mentioned barrier coat if it is an insulating thing, the quality of the material which cannot be easily corroded by the acid at the time of anodic oxidation is desirable. Moreover, when producing a start point to an insulating layer, the thing in which detailed

patterning processing is possible is desirable. concrete -- SiO2 and aluminum 2O3 etc. -- nitrides, such as oxide, and SiN, AlN, other glass, synthetic resin, a resist, etc. are possible. Although it is dependent also on the insulating layer used for these membrane formation, the vacuum forming-membranes methods, such as PVD and a CVD method, a spin coat method, a metal, the scaling method of a semi-conductor, etc. are applicable. Moreover, an anodized layer is producible also by methods of oxidizing only the front face, such as plasma oxidation and thermal oxidation.
[0047] When using this pore for device application, it is desirable to prepare the electrical installation section in the interior of pore, or to prepare an electrode layer as a growth stop layer of pore. As a film presentation, semi-conductors, such as metals, such as bulb metals, such as Ti, Nb, W, Zr, and Hf, and Pt, Cu, these alloys, and Si, are mentioned. However, in order to secure the homogeneity of pore, it is desirable that the interface of an anodized layer and an electrode layer has little irregularity.
[0048] Moreover, it becomes a process with important for application of a device putting in an endocyst object in pore. Although various kinds of approaches, such as an approach of infiltrating a liquid-like ingredient using capillarity, and an approach which the shaft orientations of pore are made to vapor-deposit, are available to the approach of putting an endocyst object into pore, for sticking an ingredient only to the interior of pore, the approach by electrodeposition is desirable.
[0049] This invention makes it possible to apply an anodic oxidation alumina with various gestalten including optical elements including quantum wire, an MIM component, a molecule sensor, coloring, a magnetic-recording medium, EL light emitting device, an electrochromic element, and a photograph nick band, an electron emission component, a solar battery, a gas sensor, abrasion resistance, the insulation-proof sex skin film, and a filter, and has the operation which extends the application range remarkably. It is especially applicable to the pore object of the nano structure of this invention with a new electron device and a new magnetic device, and optical DEBAISUHE by embedding functional materials, such as a metal, the magnetic substance, and a semi-conductor.
[0050]
[Example] An example is raised to below and this invention is explained.
[0051] Example 1 this example explains the example which produced the horizontal-type pore object using drawing 5 and drawing 8 R> 8. Drawing 5 is a sectional view showing the process in the case of producing a pore array, and drawing 8 is plant layout drawing which anodizes. For the anodization layer which 11 in drawing uses an alumina as pore (nano hole), and 12 uses as a principal component, and 13, as for a substrate and 31, a barrier coat and 14 are [the surface irregularity of an anodized layer and 32] anodized layers. Moreover, as for the power source to which the electrolytic solution and 84 impress a reaction container, and, as for a sample and 82, 85 impresses an anodic oxidation electrical potential difference for 81, as for the cathode of Pt plate, and 83, the ammeter with which 86 measures an anodic oxidation current, and 87, a thermostat and 88 are sample electrode holders among drawing 8 . Although omitted by a diagram, automatic control, the computer to measure are incorporated in the electrical potential difference and the current.
[0052] (a) The anodized layer 32 was first produced using Si substrate which has about 500nm scaling layer shown in production drawing 5 (a) of an anodized layer. That is, aluminum film was formed 350nm of thickness by the sputtering method, and the anodized layer 32 shown in drawing 5 (b) was formed on the substrate front face. Membrane formation conditions are the DC sputtering methods, and were performed for 150 W or 70 minutes. Consequently, the surface irregularity 31 has been formed in the front face of the anodized layer 32 height of about 50nm.
[0053] (b) In order to produce production, next the barrier layer of a barrier coat, aluminum film was anodized in the solution of ammonium pentaborate. The concentration of an ammonium pentaborate solution is 3wt(s)%, and was processed at the room temperature for 3 minutes with the electrical potential difference of 80V here. As a result, about 100nm of front faces of aluminum film oxidized to homogeneity, they became the barrier coat 13, and about 250nm of aluminum layers under it remained with aluminum. Moreover, flattening of a barrier coat front face and the interface of the barrier coat 13 and aluminum layer which remained was carried out like drawing 5 (c).
[0054] (c) In order to take out the field which starts anodization, next anodization, dry etching of an anodized layer and the barrier layer was carried out at right angles to a film surface by the dry etching method, and the end face was taken out. And the part of an end face was dipped into the phosphoric-acid 0.3M solution held at 5 degrees C using the anodic oxidation equipment shown in drawing 8 , the electrode was taken from the part of the opposite side, and it

anodized by 130V. After anodic oxidation termination, it was immersed in the 5wt% phosphoric acid for 60 minutes, and puncturing processing was performed.
[0055] <Evaluation> When the nano structure produced by the above-mentioned approach was observed in FE-SEM (Field Emission-Scannig Electron Microscope: field emission scanning electron microscope), it has checked that pore with little turbulence which is looked at by drawing 5 (d) was formed 230nm of ****, and like hole diameter 150nm.
[0056] It is SiO2 to the anodized layer upper part without forming a barrier coat for a comparison. When same pore formation was carried out by the sample which formed the film 50nm of thickness by the sputtering method, it was confused like drawing 6 .
[0057] After example 2 this example removes a barrier coat, it is explained [production / horizontal-type pore] using drawing 5 about how to produce an insulating layer.
[0058] First, it forms to a barrier coat like an example 1 (drawing 5 (c)). And when it was immersed into the mixed solution of a chromic acid and phosphoric acid for 2 hours and the barrier layer was removed, the irregularity of an anodized layer front face had become 1/3 or less magnitude from the surface irregularity 31 seen after membrane formation. And it is SiO2 to a front face. 50nm formed membranes. Membrane formation is the RF sputtering method and was performed for 100 W or 5 minutes.
[0059] And after processing the end face like the example 1 for anodic oxidation, when it anodized, the porous coat of the horizontal type which has pore with little the same turbulence as an example 1 was formed.
[0060] After example 3 this example removes a barrier coat, it is explained [production / vertical mold pore] using drawing 3 about how to produce a porous coat.
[0061] (a) The anodized layer 32 was first produced using Si substrate without the scaling layer shown in production drawing 3 (a) of an anodized layer. That is, aluminum film was formed 500nm of thickness by the sputtering method, and the anodized layer 32 shown in drawing 3 R> 3 (b) was formed on the substrate front face. Membrane formation conditions are the DC sputtering methods, and were performed for 150 W or 100 minutes. Consequently, the surface irregularity 31 has been formed in the front face of the anodized layer 32 height of about 70nm.
[0062] (b) In order to produce removal, next a barrier coat as production of a barrier coat, aluminum film was anodized in the solution of ammonium pentaborate. The concentration of an ammonium pentaborate solution is 3wt(s)%, and was processed at the room temperature for 3 minutes with the electrical potential difference of 100V here. As a result, about 130nm of front faces of aluminum film oxidized to homogeneity, they became the barrier coat 13, and about 370nm of aluminum layers under it remained with aluminum. Moreover, flattening of a barrier coat front face and the interface of the barrier coat 13 and aluminum layer which remained was carried out like drawing 3 (c).
[0063] And when it was immersed into the mixed solution of a chromic acid and phosphoric acid for 2 hours and the barrier layer was removed, the irregularity of an anodized layer front face had become 1/3 or less magnitude from the surface irregularity 31 seen after membrane formation.
[0064] (c) The front face was dipped into the oxalic acid 0.3M solution held at 15 degrees C using anodic oxidation and the anodic oxidation equipment shown in drawing 8 , the electrode was taken from the substrate side, and it anodized by 40V. After anodic oxidation termination, it was immersed in the 5wt% phosphoric acid for 40 minutes, and puncturing processing was performed.
[0065] <Evaluation> When the nano structure produced by the above-mentioned approach was observed in FE-SEM, it has checked that pore with little turbulence which is looked at by drawing 3 (e) was formed 100nm of ****, and like hole diameter 60nm. When it anodized as it is and pore formation was carried out without forming a barrier coat for a comparison, pore was confused like drawing 7 (b).
[0066] After example 4 this example removes a barrier coat partially by the FIB method, it is explained [production / of vertical mold pore] using drawing 4 about how to produce a porous coat.
[0067] First, it forms to a barrier coat like an example 3 (drawing 4 (c)). However, the barrier coat was made into 50nm thickness. And the dot of the shape of a honeycomb with a spacing of 100nm was drawn on the porous coat front face using the FIB method, and the structure which produces the barrier coat removal part 41 and is shown in drawing 4 (d) was processed. As Ga ion at this time became a repeat with a spacing of 100nm using 30nm of diameters of an ion beam, ion current 20pA, and a focused ion beam with an acceleration voltage of 30kV, the porous coat was made to penetrate partially by irradiating a focused ion beam in the shape of a dot at a workpiece.
[0068] Anodizing was performed for the sample produced in the above process using the anodic oxidation equipment

of drawing 8 . In this example, the acid electrolytic solution was used as the oxalic acid water solution of 0.3M, the solution was held at 15 degrees C with the constant temperature bath, and the anodic oxidation electrical potential difference was set to 40V. after anodizing -- a sample -- 5wt(s)% -- the path of pore was extended by dipping for 40 minutes into a phosphoric-acid solution.
[0069] As a result of carrying out FE-SEM observation of the sample produced by the <evaluation> above-mentioned producing method, the regular vertical mold pore array object as shown in drawing 4 (e) was formed. At this time, pore spacing was about 100nm and pore size was about 60nm.
[0070] After removing a barrier coat and example 5 this example forms a start point by the FIB method on an anodized layer about vertical mold pore production, it explains how to produce a porous coat.
[0071] First, it carries out to removal of a barrier coat like an example 3. And the dot of the shape of a honeycomb with a spacing of 100nm was drawn in the anodized layer using the FIB method, and the start point was processed on the anodized layer. Using 30nm of diameters of an ion beam, ion current 10pA, and a focused ion beam with an acceleration voltage of 30kV, as Ga ion at this time became a repeat with a spacing of 100nm, it produced the crevice on the anodized layer by irradiating a focused ion beam in the shape of a dot at a workpiece.
[0072] Anodizing was performed for the sample produced in the above process using the anodic oxidation equipment of drawing 8 . In this example, ******** considered as the oxalic acid water solution of 0.3M, the solution was held at 15 degrees C with the constant temperature bath, and the anodic oxidation electrical potential difference was set to 40V. after anodizing -- a sample -- 5wt(s)% -- the path of pore was extended by dipping for 40 minutes into a phosphoric-acid solution.
[0073] As a result of carrying out FE-SEM observation of the sample produced by the <evaluation> above-mentioned producing method, the regular vertical mold pore array object was formed like the example 4. At this time, pore spacing was about 100nm and pore size was about 60nm.
[0074] Example 6 this example produces an insulating layer, after removing a barrier coat, and it explains [production / vertical mold pore] it using drawing 4 about how to carry out FIB of the start point. First, it forms to a barrier coat like an example 4 (drawing 4 (c)). And when it was immersed into the mixed solution of a chromic acid and phosphoric acid for 2 hours and the barrier layer was removed, the irregularity of an anodized layer front face had become 1/3 or less magnitude from the surface irregularity 31 seen after membrane formation. And it is SiO_2 to a front face. 50nm formed membranes. Membrane formation is the RF sputtering method and was performed for 100 W or 5 minutes.
[0075] And the surface insulating layer was made to penetrate to an anodized layer in the shape of a honeycomb dot by this FIB method on the same conditions as partial removal of the barrier coat in an example 4 (drawing 4 (d)). Anodizing was performed for the sample produced in the above process like the example 4, and processing which extends the path of pore was performed.
[0076] As a result of carrying out FE-SEM observation of the sample produced by the <evaluation> above-mentioned producing method, the regular vertical mold pore array object was formed like the example 4. At this time, pore spacing was about 100nm and pore size was about 60nm.
[0077]
[Effect of the Invention] As explained above, the following effectiveness is acquired by this invention.
(1) Flattening of the irregularity suited the anodized layer front face and the interface is carried out by ********, and the turbulence and the defect of pore which are produced by anodic oxidation as a result can be lessened.
(2) Moreover, although flattening of the irregularity of an anodized layer front face is carried out, by electrolytic polishing, aluminum part made into a sacrifice can offer greatly the manufacture approach which lessens a sacrifice part for flattening which was not made by aluminum film.
(3) The new regular nano structure produced with the application of these techniques can be offered.
[0078] These make it possible to apply an anodic oxidation alumina with various gestalten, and extend the application range remarkably. The nano structure of this invention can also be used as the base material of the further new nano structure, mold, etc., although it is usable as a functional material in itself.

[Translation done.]

* NOTICES *

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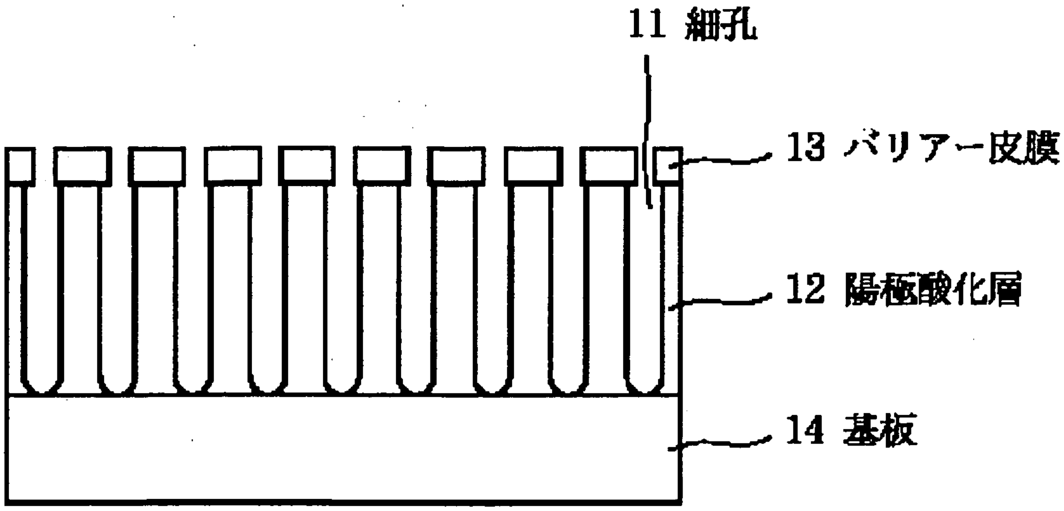
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the sectional view showing the nano structure which has the vertical mold pore of this invention.
[Drawing 2] It is the sectional view showing the nano structure which has the horizontal-type pore of this invention.
[Drawing 3] It is drawing showing the making process of the vertical mold pore object from which the barrier coat was removed.
[Drawing 4] It is drawing showing the making process of the vertical mold pore object which left the barrier coat.
[Drawing 5] It is drawing showing the making process of a horizontal-type pore object.
[Drawing 6] It is the sectional view showing the nano structure which has the horizontal-type pore of the conventional example.
[Drawing 7] It is the sectional view showing the nano structure which has the vertical mold pore of the conventional example.
[Drawing 8] It is drawing showing the equipment which performs anodizing.
[Drawing 9] It is the sectional view showing the nano structure which has the vertical mold pore of the conventional example.
[Description of Notations]
11 Pore
12 Anodic Oxidation Layer
13 Barrier Coat
14 Substrate
21 Middle Barrier Coat
22 Up Barrier Coat
31 Surface Irregularity
32 Anodized Layer
41 Removal Part
61 Pore Bottom Insulating Layer
62 Up Insulating Layer
71 Heights
72 Crevice
81 Sample
82 Cathode
83 Electrolytic Solution
84 Reaction Container
85 Power Source
86 Ammeter
87 Thermostat
88 Sample Electrode Holder
91 Aluminum Plate

[Translation done.]



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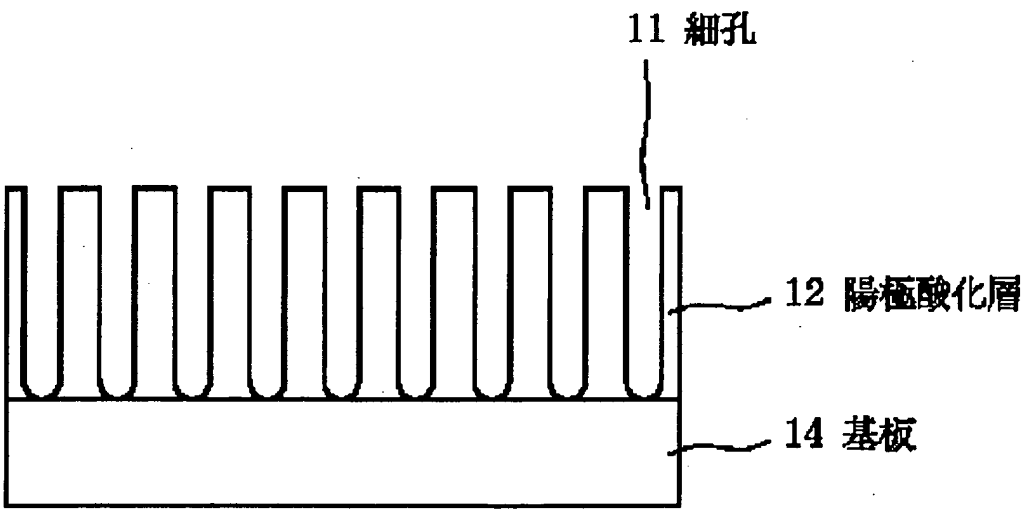

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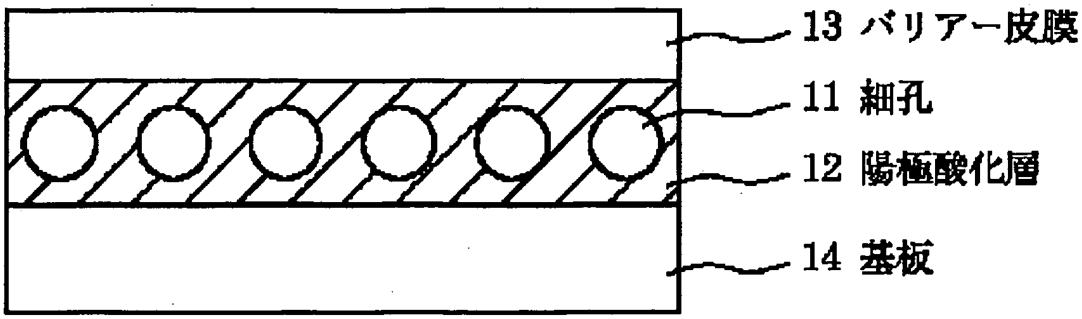
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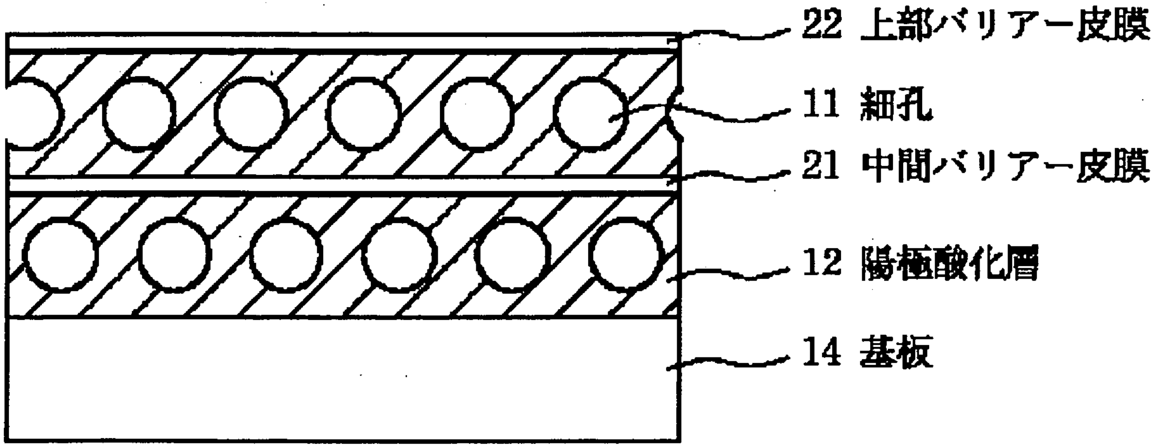
11 細孔
12 陽極酸化層
14 基板

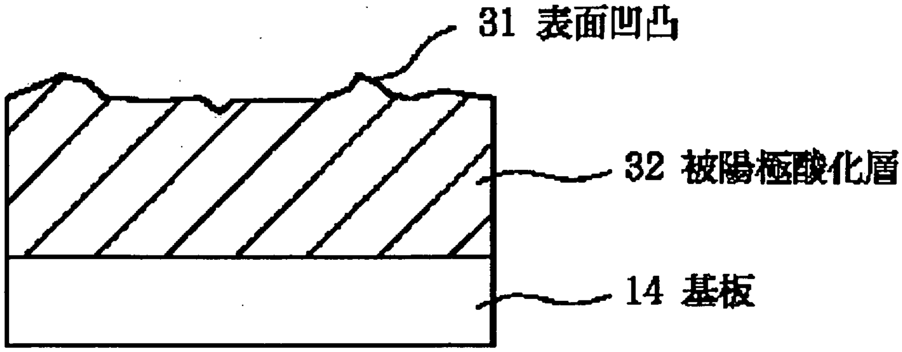
(a)


22 上部バリアー皮膜
11 細孔
21 中間バリアー皮膜
12 陽極酸化層
14 基板

(b)

(a)

(b)



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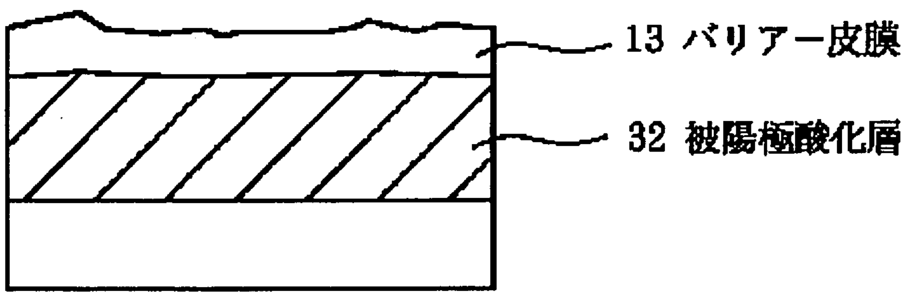

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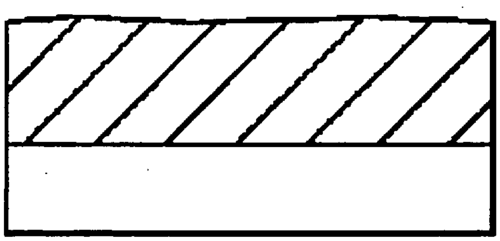

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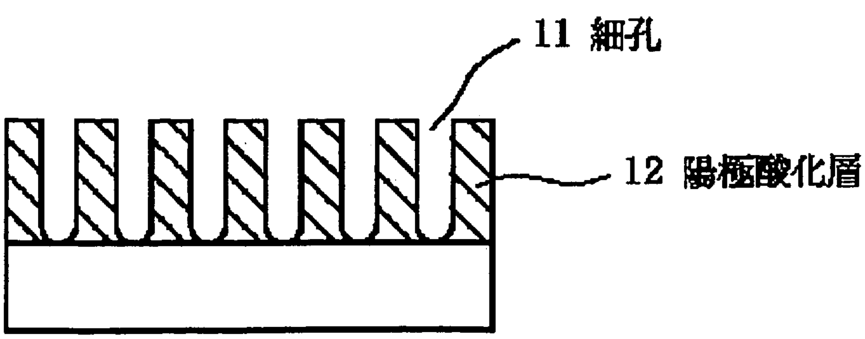
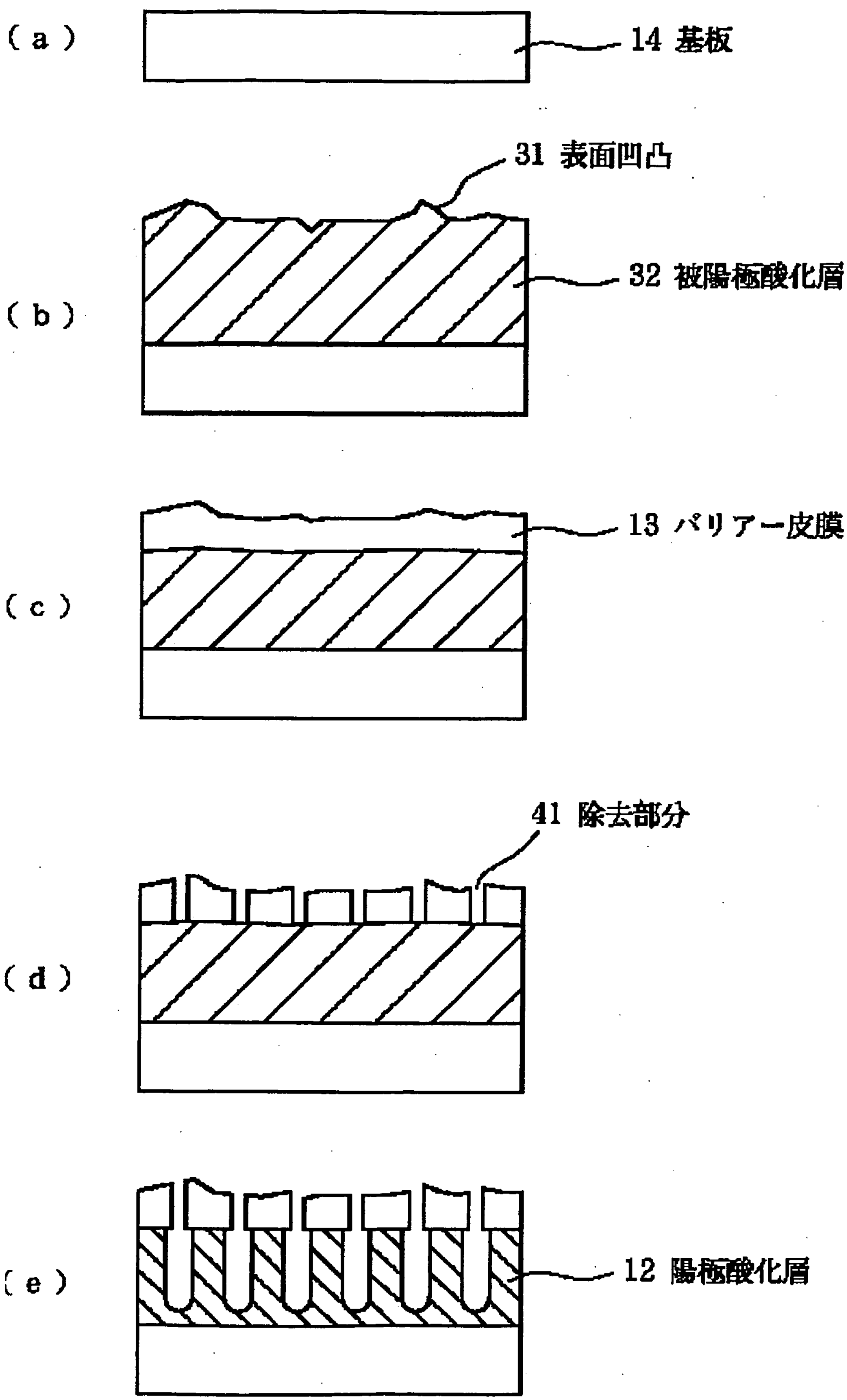
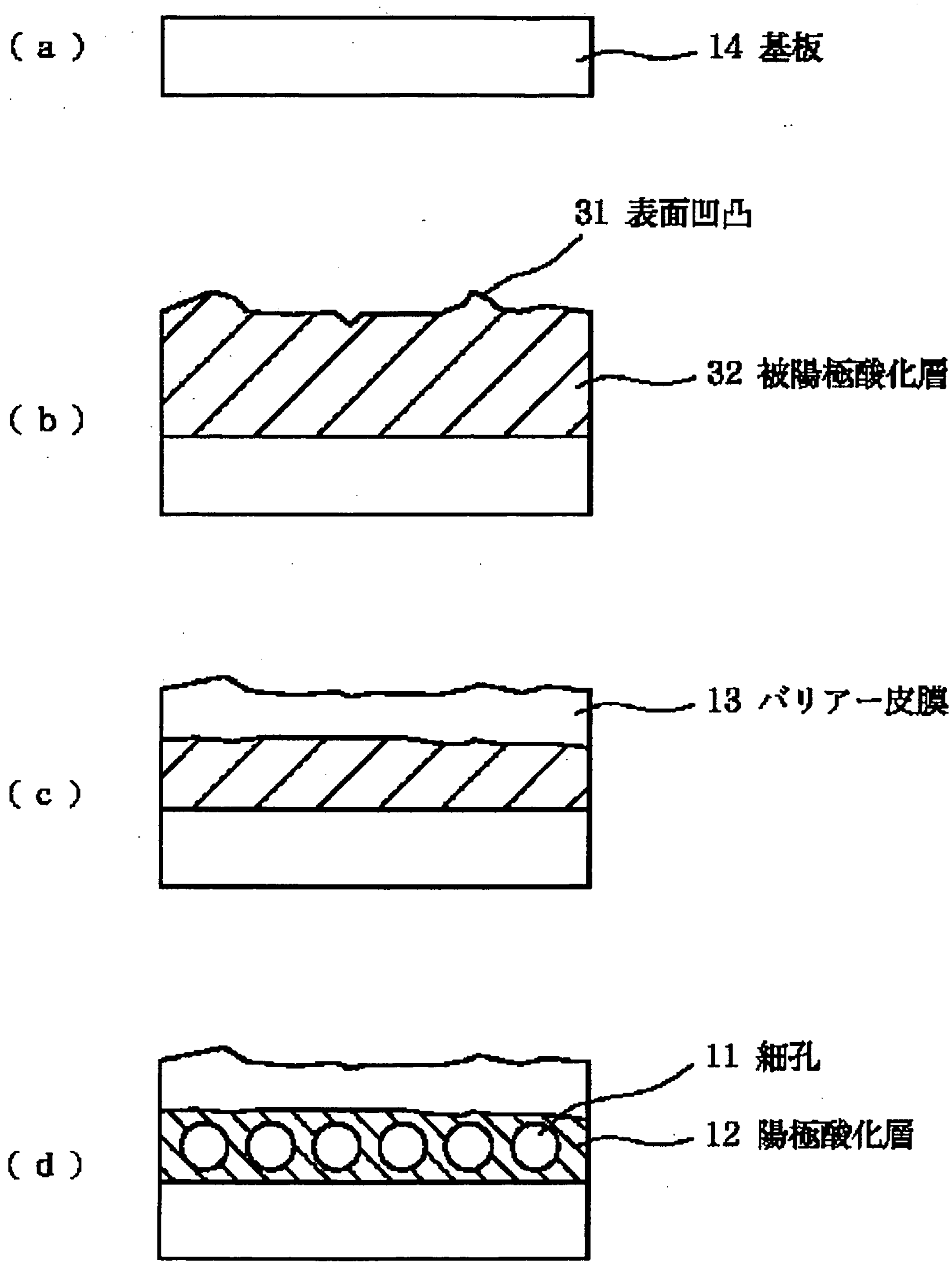
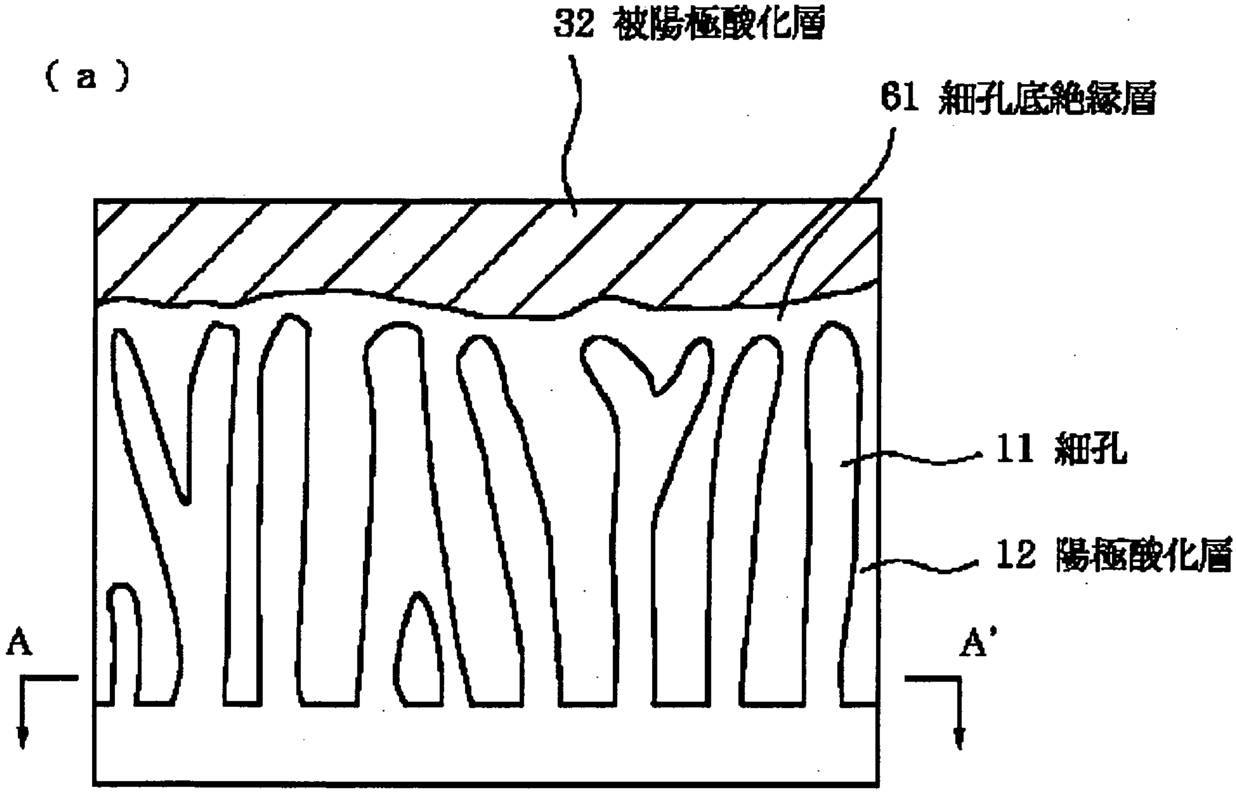


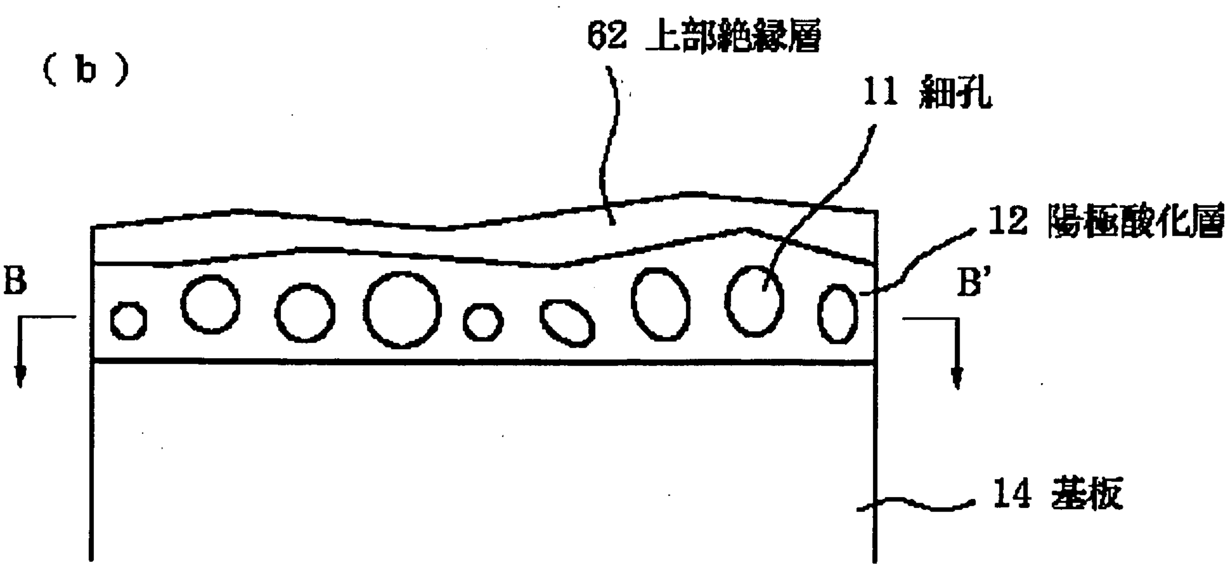

（a）
14 基板
31 表面凹凸
（b）
32 被陽極酸化層
（c）
13 バリアー皮膜
41 除去部分
（d）
（e）
12 陽極酸化層


(a)
14 基板
31 表面凹凸
32 被陽極酸化層
(b)
13 バリアー皮膜
(c)
11 細孔
12 陽極酸化層
(d)

（ａ）


32 被陽極酸化層
61 細孔底絶縁層
11 細孔
12 陽極酸化層
A
A'

（ｂ）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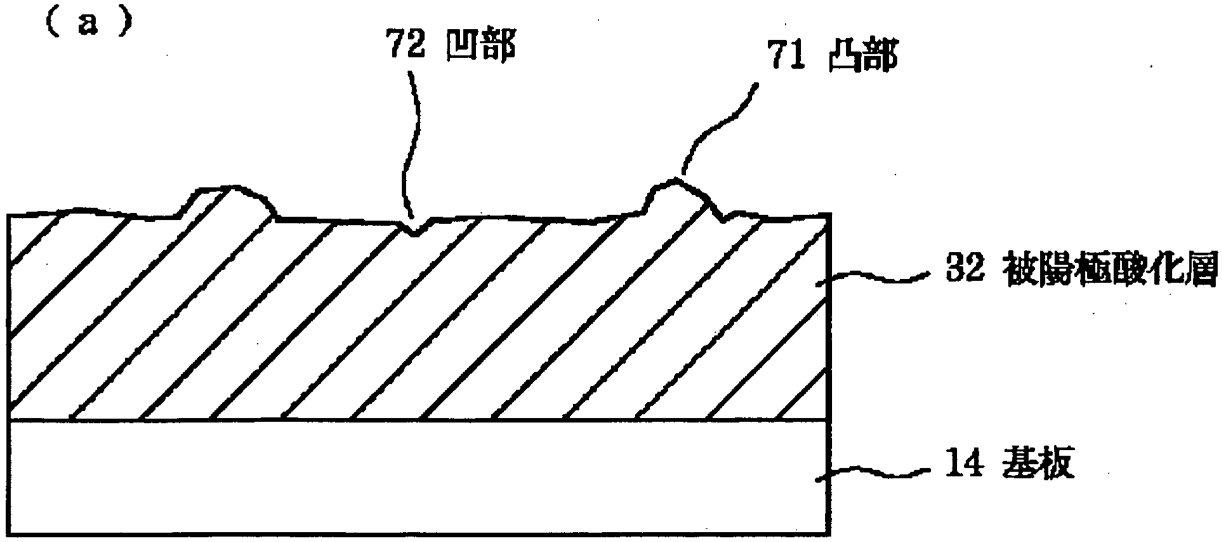
11 細孔
12 陽極酸化層
B
B'
14 基板

（a）



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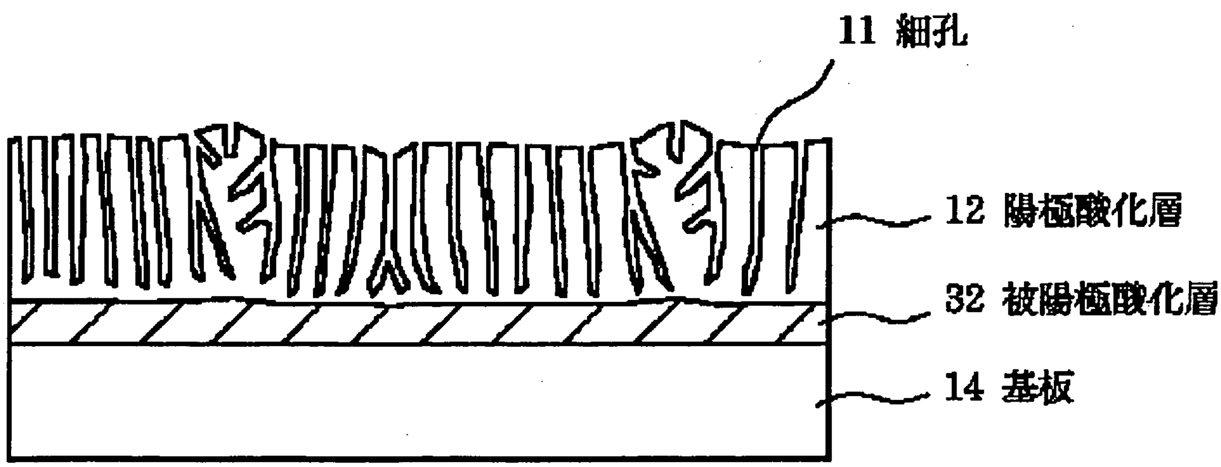
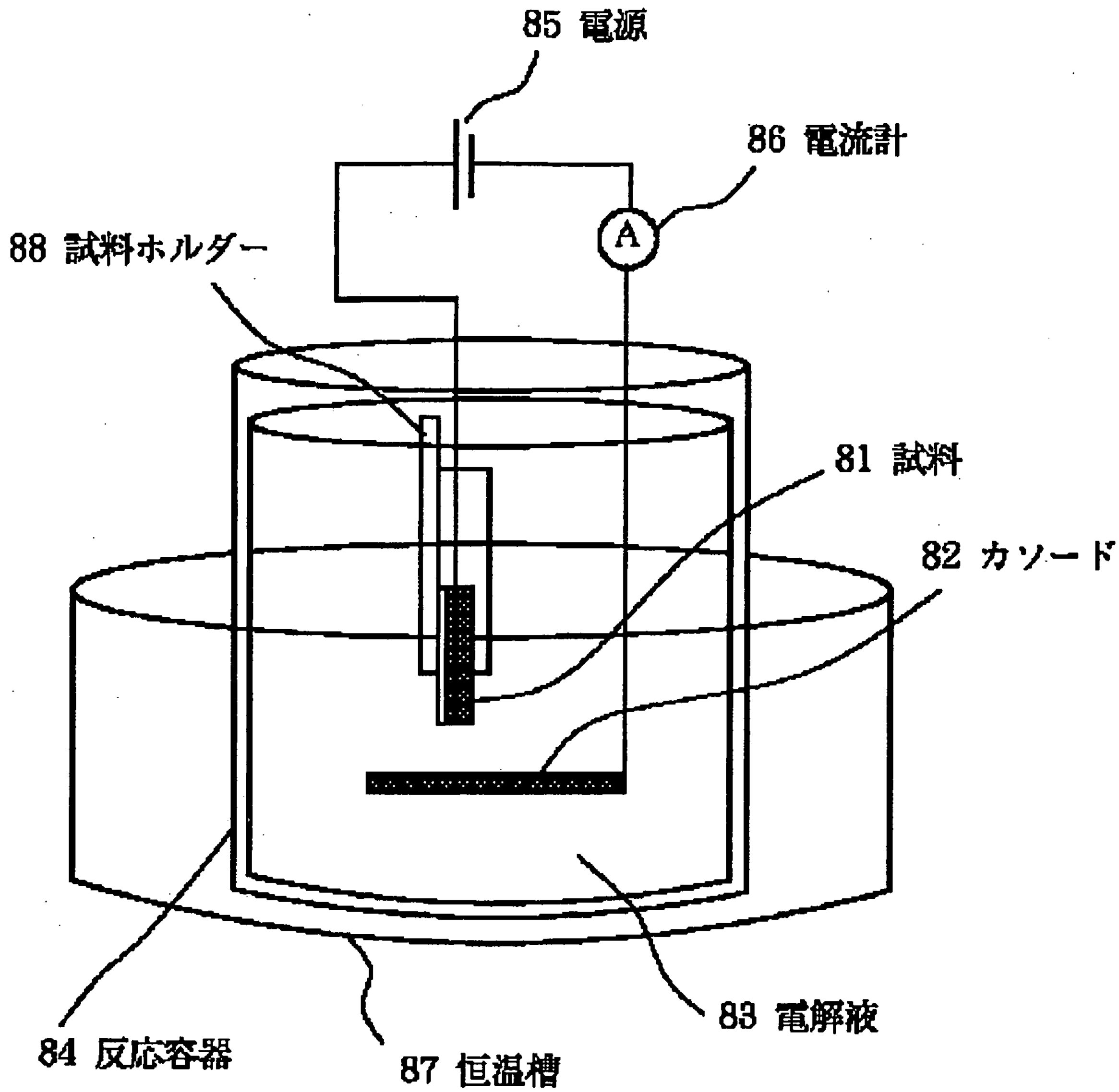
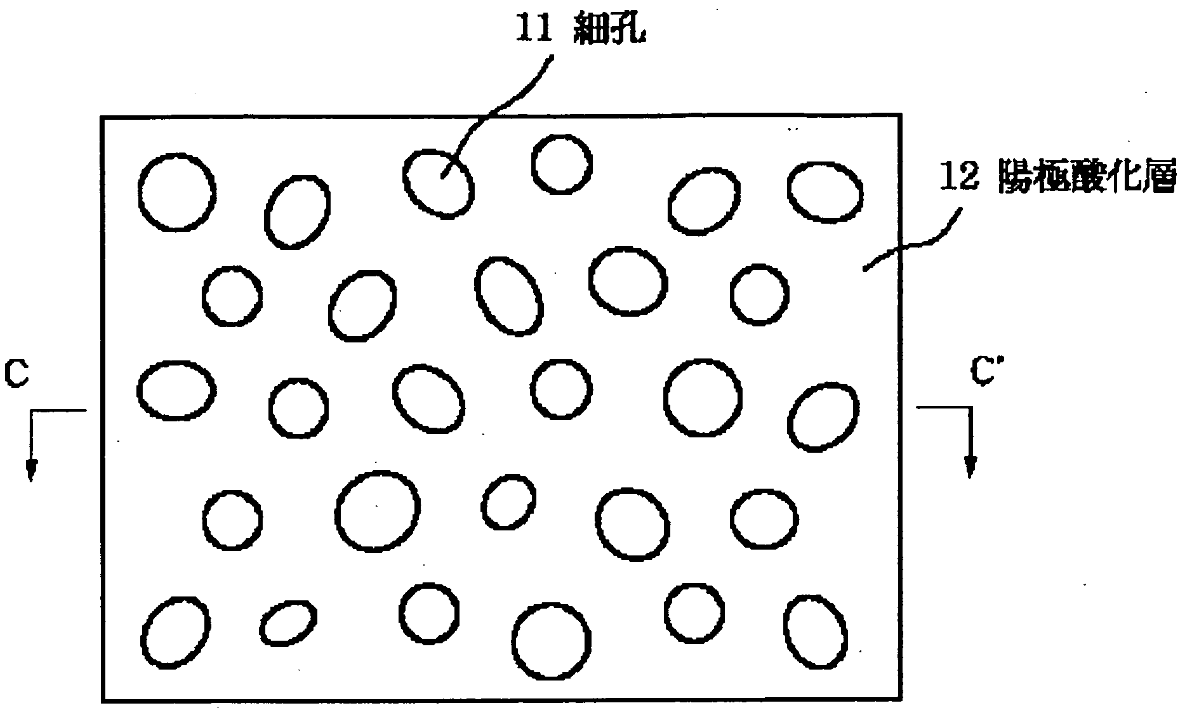
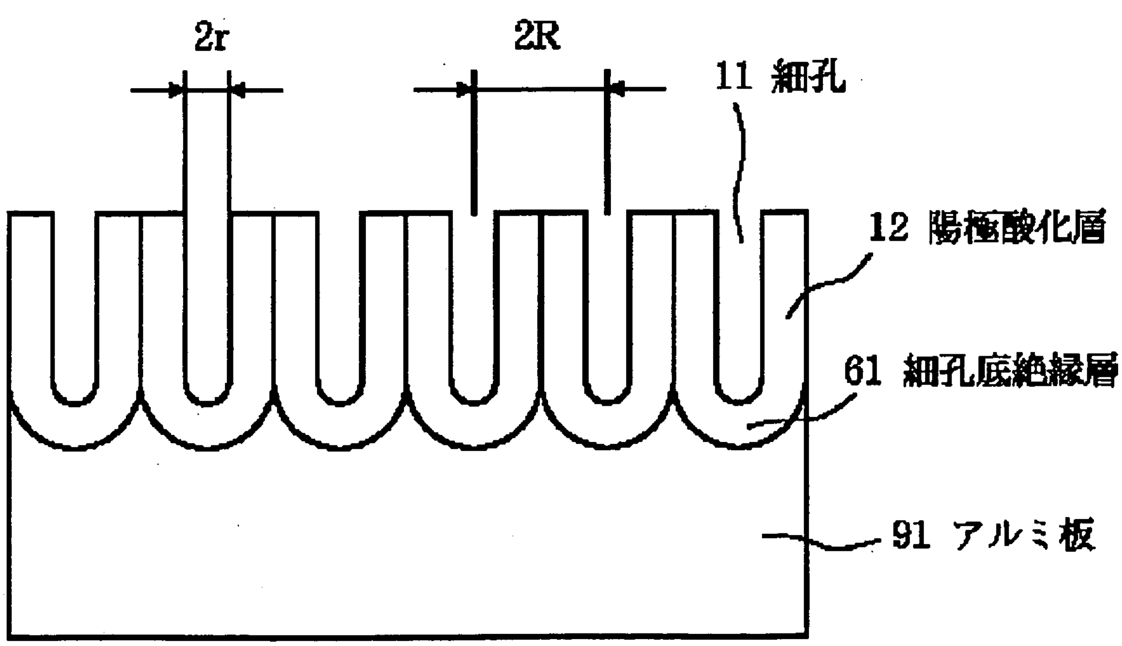




85 電源
86 電流計
88 試料ホルダー
81 試料
82 カソード
84 反応容器
87 恒温槽
83 電解液



（ a ）



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